

# Thermal Behaviors and Flame-Retardancy of Styrene–Ethylene–Butadiene–Styrene–Block Copolymer Containing Various Additives

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**ABSTRACT:** The thermal behaviors and the flame-retardancy of styrene–ethylene–butadiene–styrene–block copolymer containing various additives were studied. The combustion was measured by the Underwriter laboratory (UL) test and cone calorimeter test and thermogravimetric analysis and program-mass spectroscopy were applied to analyze the thermal behaviors. The blend with halogen additives showed the best result in the UL test. However, the blend with red-phosphorous was the best in the cone calorimeter test. As the styrene sequence in the copolymer tended to degrade at a lower temperature, the major scission prod-

ucts spouted out from the polymer surface originated from polystyrene. The shorter the ignition times of the blends with red-phosphorous were, the lower the peak heat release rates were. It was an interesting phenomenon because it suggested that the chemical structure of the residue changed to more stable polymers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 156–161, 2007

**Key words:** thermal behavior; flame-retardancy styrene–ethylene–butadiene–styrene–block copolymer; additives; red-phosphorous

## INTRODUCTION

Styrene–ethylene–butadiene–styrene–block copolymer (SEBS) is an excellent material that is commercially exploited as rubber-like materials in various fields because of its superb elastic properties. In recent years, it has also been used as soft-type plastics. On the other hand, with the increasing concern for safety, the flame-retardancy of the block copolymer is becoming a necessity.

Halogenated flame-retardants with antimony oxide have been known as effective flame-retardants for the copolymer.<sup>1</sup> However, the polymer blended with halogen compounds have recently been regarded as undesirable materials with the danger of environmental pollution. In particular, as the boycott movement against halogen compounds became active in Europe,<sup>2</sup> many efforts have been made to develop nonhalogen flame-retardants. Inorganic compounds, such as aluminum hydroxide,<sup>3</sup> organic phosphates,<sup>4</sup> red-phosphorous,<sup>5</sup> ammonium polyphosphate,<sup>6</sup>

silicone compounds,<sup>7</sup> and nano-composite made by clays<sup>8</sup> have been studied and developed for industrial use as typical flame-retardants.

SEBS is one of the most difficult polymers, whose flame-retardancy can be improved by the compounds listed earlier because the butadiene and styrene units in the polymer are very flammable.<sup>9,10</sup> In an attempt to provide a basis toward understanding flame-retardancy, we tried to study the flame-retardancy as well as the thermal degradations on the basis of the articles on the degradation of polyethylene, which decomposes through similar paths as those of polybutadiene (PB) and polystyrene (PS).

Studies on the thermal degradation of polyethylene (PE) have been conducted since the 1940s and the kinetics, the assignment of the scission products, and the degradation paths have been elucidated.<sup>11–15</sup>

The degradation of *cis*-1,4-polybutadiene has also been studied by several researchers. The monomer, butadiene, and the dimer, 4-vinylcyclohexene, were observed as the major scission products.<sup>16,17</sup>

On the other hand, the degradation of PS has also been studied by many researchers and the paths of 1,5-transfer and de-polymerization are observed as the major paths.<sup>18–20</sup>

In this study, the data of the flame-retardancy and the thermal degradation of SEBS with various flame-

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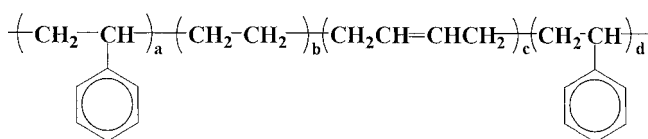


Figure 1 Chemical structure of SEBS.

retardants by the methods of thermal analyses and combustion tests have been analyzed.<sup>21,22</sup>

## EXPERIMENTAL

### Materials

The SEBS was provided by Asahi Kasei, Japan, and the sample grade was SEBS-1. Although the molecular weight is low and the melt flow rate is high, the elastomer has a high modulus, high strength, good weatherability, antiaging property, antichemicals, and excellent electric performance. The miscibility that is important for industrial applications with PS and polyolefin is so good that the impact strength of their alloy is high. The chemical structure of the SEBS is shown in Figure 1 and the content of styrene is 30 wt %.

### Blend preparation

The SEBS and the PS were mixed with the flame-retardants listed in Tables I and II by tumbling and the mixtures were fed into a 26-mm twin screw extruder manufactured by Kurimoto Tekko, Japan (S-1) at 200°C. The L/D (the ratio of the length and the diameter) was designed at 10.2 and the rotation rate was 80 rpm. The extrudates were comminuted into a pellets processor. The pellets were then placed into the mold of a press machine, manufactured by Toyo Seiki, Japan (MP-SNH), at 200°C to be formed into standard test specimens. The pressure program was from (300 s under 20 kg) via (60 s under 0 kg) to (300 s under 100 kg).

### Measurements

Burning and ignition times were performed according to the Underwriter laboratory (UL-94) test, well known as a burning test for plastics. A cone calorimeter manufactured by Toyo Seiki (Cone Calorimeter type-3) was used to measure the heat release rate and other details of flammability. Babrauskas and Huggett developed the cone calorimeter in 1982 by applying Thornton's principle by which the combustion heat of almost all organic materials were 13.1 kJ/g-O<sub>2</sub> and the error range was less than 5%.<sup>23-25</sup>

TGA-50 manufactured by Shimadzu, Japan, was used for thermal gravimetric analysis (TGA). Experiments were carried out on 5.0 mg of the samples under nitrogen at a flow rate of 50 mL/min and a furnace-heating

TABLE I  
List of Flame-Retardants Blended  
with SEBS, PS, and PE

| No. | Flame-retardant             | Code                           | Amount (wt %) |
|-----|-----------------------------|--------------------------------|---------------|
| 1   | Neat                        | Neat                           | –             |
| 2   | Decabromodiphenyl oxide     | DBDPO                          | 10            |
|     | Antimony trioxide           | Sb <sub>2</sub> O <sub>3</sub> | 5             |
| 3   | Red-phosphorous             | Red-P                          | 3             |
| 4   | BisphenolAbiscesylphosphate | BBC                            | 10            |

rate of 90°C/min up to 800°C. The rate was much higher than that in general degradation experiments because the main purpose of this study was to analyze the degradation during fire when the elevating rate of the temperature was supposed to be about 100°C/min.

A gas chromatograph and mass spectrometry manufactured by Shimadzu, Japan (GCMS-QP5000) was applied to analyze the fragmentation from the pyrolyzer. The procedures were achieved according to the usual way as in the degradation experiments of plastics. The interface temperature between the pyrolyzer and the gas chromatograph was 280°C, a 27 m-length capillary column was used and the linear velocity of helium as a carrier gas was 26.4 cm/s. The minimum and the maximum mass number were 45 and 500, respectively.

## RESULTS

### Flammability

The results of the UL test and the cone calorimeter test are listed in Table III. The Neat specimen with-

TABLE II  
List of Flame-Retardants Blended with SEBS

| No. | Flame-retardant                                    | Code                           | Amount (wt %) |
|-----|--|--------------------------------|---------------|
| 1   | Neat   | Neat                           | –             |
| 2   | Decabromodiphenyl oxide                            | DBDPO                          | 10            |
|     | Antimony trioxide                                  | Sb <sub>2</sub> O <sub>3</sub> | 5             |
| 3   | Tetrabromobisphenol A-bis (2,3-dibromopropylether) | TBA-DB                         | 15            |
| 4   | Tetrabromobisphenol S-bis (2,3-dibromopropylether) | TBS-DB                         | 15            |
| 5   | Red-phosphorous                                    | Red-P                          | 3             |
| 6   | Red-phosphorous                                    | Red-P                          | 4             |
| 7   | Red-phosphorous                                    | Red-P                          | 4             |
|     | Carbon black                                       | Carbon black                   | 1             |
| 8   | BisphenolAbiscesyl phosphate                       | BBC                            | 15            |
| 9   | Silicon dioxide                                    | SiO <sub>2</sub> (Porous)      | 5             |
| 10  | Copper ethylenediamine tetraacetic acid            | Cu-EDTA/SiO <sub>2</sub>       | 5             |
| 11  | 2,2'-bipyridyl copper                              | Cu-bpy/SiO <sub>2</sub>        | 5             |
| 12  | Acetylacetonatoiron                                | Fe-acac/SiO <sub>2</sub>       | 5             |
| 13  | Melamine Cyanulate                                 | Melamine Cyanulate             | 5             |

TABLE III  
Results of the UL-Test and Cone Calorimeter Test for Flammability

| Flame-retardant                      | Amount (wt %) | UL combustion test  |                               |                 | Cone calorimeter analysis                    |   |                     |
|--------------------------------------|---------------|---------------------|-------------------------------|-----------------|--|---|---------------------|
|                                      |               | Ignition time (sec) | Flaming combustion time (sec) | Drip time (sec) | Peak heat release rate (kW m <sup>-2</sup> ) | Total heat released (MJ m <sup>-2</sup> ) | Ignition time (sec) |
| Neat                                 | –             | 7.3                 | (244.2)                       | 6.1             | 1997.5                                       | 112.0                                     | 30.4                |
| DBDPO/Sb <sub>2</sub> O <sub>3</sub> | 10/5          |                     | Nonignition                   |                 | 1874.0                                       | 76.4                                      | 38.5                |
| TBA-DB                               | 15            | 5.7                 | 103.0                         | 5.8             | 2281.4                                       | 79.8                                      | 33.6                |
| TBS-DB                               | 15            | 8.9                 | 24.6                          | 3.4             | 2061.8                                       | 82.4                                      | 34.8                |
| Red-P                                | 3             | 11.5                | 18.9                          | 1.8             | 1432.7                                       | 82.4                                      | 28.9                |
| Red-P                                | 4             | 8.9                 | 15.9                          | 1.6             | 1407.6                                       | 74.1                                      | 25.5                |
| Red-P/Carbon black                   | 4/1           | 7.4                 | 53.7                          | 4.4             | 1340.9                                       | 72.0                                      | 21.0                |
| BBC                                  | 15            | 9.9                 | 46.5                          | 3.8             | 1597.7                                       | 84.2                                      | 34.8                |
| SiO <sub>2</sub> (Porous)            | 5             | 4.5                 | (187.1)                       | 5.3             | 1839.8                                       | 95.6                                      | 26.1                |
| Cu-EDTA/SiO <sub>2</sub>             | 5             | 5.1                 | (216.2)                       | 4.0             | 1847.1                                       | 93.6                                      | 26.4                |
| Cu-bpy/SiO <sub>2</sub>              | 5             | 5.1                 | (163.8)                       | 5.9             | 2030.3                                       | 100.2                                     | 33.4                |
| Fe-acac/SiO <sub>2</sub>             | 5             | 4.5                 | (254.5)                       | 6.9             | 1763.6                                       | 113.2                                     | 30.9                |
| Melamine cyanurate                   | 5             | 4.9                 | (239.6)                       | 5.1             | 1652.6                                       | 91.7                                      | 20.5                |

out flame-retardants burnt well and the peak heat release rate (PHRR) of the cone calorimeter was about 2000 kW/m<sup>2</sup>. On the other hand, the blend with DBDPO/Sb<sub>2</sub>O<sub>3</sub> showed excellent flame-retardancy in the UL test whereas the PHRR was the same as that of the Neat specimen.

Other specimens blended with various flame-retardants except DBDPO/Sb<sub>2</sub>O<sub>3</sub> ignited and half of them burnt out completely. However, the PHRR of the several specimens were lower than that of the Neat.

In particular, the flaming combustion times of the blends with Red-P and BBC were remarkably shorter than that of the Neat specimen. The same tendency of the flame-retardancy was observed in the cone calorimeter test. The PHRR of the blend with Red-P and Carbon black was 1341 kW/m<sup>2</sup>, which showed the minimum value among all specimens including the Neat and the blend with DBDPO/Sb<sub>2</sub>O<sub>3</sub>.

In Figure 2, the profiles of the heat release rates observed in the cone calorimeter were depicted. The peak values of the blends were lower than that of the Neat specimen. However, the shapes themselves were almost the same.

### Thermogravimetric analysis

TGA curves of all samples, useful for the analysis of flame-retardancy, are depicted in Figure 3. The thermal degradation started at 450°C and the temperature of 50% degradation was 510°C. The amount of the residue at 600°C was very small. The degradation accelerated remarkably by blending with BBC and slightly by blending with TBA-DB and TBS-DB.

On the other hand, higher degradation temperatures were observed for the blends with Melamine cyanurate, copper, and ferric complexes. Although

the flame-retardancy of the blend with Red-P was improved, no difference was observed in TGA.

### Mass spectroscopy

To observe the chemical structure of the scission products, some of the blends were used for the measurement of the mass spectroscopy. The pyrogram of the Neat specimen is shown in Figure 4 where very simple signals were observed. The large signals were assigned as the monomer and the trimer of styrene and some volatile products were observed in the region of the low molecular weight.

The assigned products are listed in Figure 3. The aliphatic hydrocarbons of C<sub>4</sub> and C<sub>8</sub> would be the scission products from the PB sequence. The five aromatic scission products were from the PS sequence.

The distributions of the scission products are plotted in Table IV. The major product was the monomer and its contents were more than 70%. The sec-

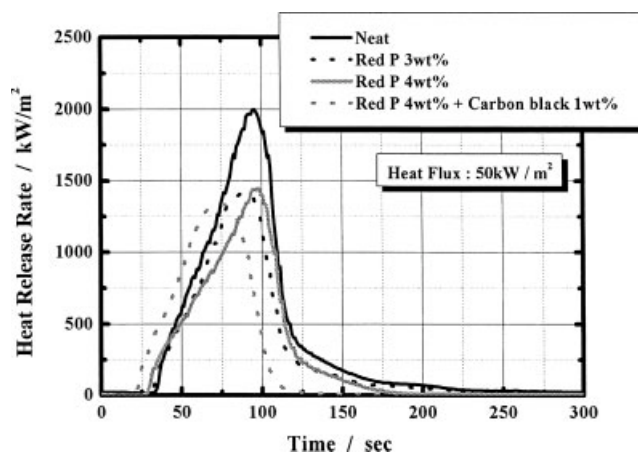


Figure 2 Heat release rate of the Neat specimen and the blends with Red-P.

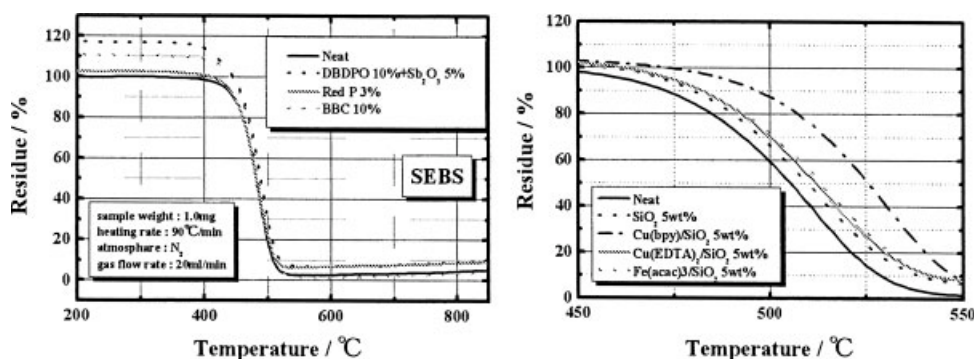


Figure 3 TGA curves of the Neat specimen and the blends (left: traditional flame-retardants, right: new ones).

ond largest peak was the trimer. Approximately 90% of the scission products were occupied by the two chemicals.

As the content of PS in the polymer was 30%, the sequence of the PS in the copolymer was a minor component. But the two major products were the fragments of the PS sequence. It suggested that the degradation of PS sequence was faster than that of the PB sequence.

## DISCUSSION

Two interesting points are in the combustion phenomena of this copolymer. One is the effect of the PB sequence in the copolymer chain to the thermal degradation. The other is the phosphorous effect to the flame-retardancy, in particular, the dependence of the ignition time on the PHRR.

First, the degradation profiles and the scission products of PS and the copolymer will be compared.

The content of PS was 30%, but the scission products of SEBS from the PS sequence was about 90% as shown in Table IV. On the other hand, the sum of the amount of the monomer, the dimer and the trimer was below 90% even for pure PS. So, only the PS part in the copolymer was considered to degrade.

The amount of the styrene dimer in the scission products of SEBS was much lower than that in the products of PS Table V. Only 1.5% was observed in the former fragments whereas 13.4% was in the PS scission products.

1,5-transfer is generally accepted as a major degradation path of PS. Through it, the ratio of the monomer, the dimer and the trimer is expected to be about 70 : 10 : 20. The different ratio of the dimer suggests the other path in addition to 1,5-transfer exists.

The amounts of the trimer of the blends with three kinds of additives are also different between the SEBS and the PS. Although, the reason cannot be found, the degradation of the PS depends on the PS sequence and the additives.

As the TGA curves of PE shown in Figure 5 show, the 50% degradation temperatures are about 500°C, which are higher than that of PS by 20°C. As for the PB sequence, B1 and B2 in Table IV are the scission products of the PB sequence,<sup>26</sup> and the sum of the contents is about 3%, which is one thirtieth when compared with the scission products of PS. Both thermal degradation data suggest that the PS sequence degrades faster and it influences the chemically structural change of PE and PB sequences.

The following discussion will be done on the basis of the earlier results of the thermal degradation of SEBS, PE, PB, and PS.

Generally speaking, the lower the degradation temperature is and the faster the ignition time is, the smaller the PHRR is. During combustion, the scission products whose boiling points are below the combustion temperature spout out from the polymer and react with oxygen in the oxidation site. When the degradation temperature is low it means that the amount of the scission product is larger. So, the total

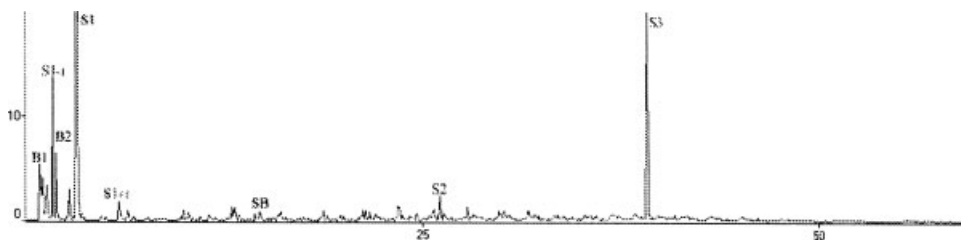


Figure 4 Pyrogram of the Neat specimen at 550°C.

TABLE IV  
Scission Products of SEBS Assigned by Mass Spectrometry

|                                      | Molecular structure | Amount (wt %) | Decomposition products |                  |     |      |                  |     |     |      |
|--------------------------------------|---------------------|---------------|------------------------|------------------|-----|------|------------------|-----|-----|------|
|                                      |                     |               | B1                     | S1 <sub>-1</sub> | B2  | S1   | S1 <sub>+1</sub> | SB  | S2  | S3   |
| Neat                                 | —                   | —             | 1.1                    | 3.3              | 1.7 | 67.1 | 1.5              | 0.9 | 1.7 | 22.8 |
| DBDPO/Sb <sub>2</sub> O <sub>3</sub> |                     | 15            | 1.1                    | 3.5              | 1.8 | 66.8 | 1.0              | 0.8 | 2.2 | 22.7 |
| Red-P                                |                     | 3             | 1.0                    | 3.3              | 1.7 | 71.4 | 2.4              | 0.9 | 1.7 | 17.6 |
| BBC                                  |                     | 10            | 1.3                    | 3.8              | 1.9 | 75.6 | 1.6              | 1.0 | 1.6 | 13.1 |

enthalpy of the oxidation by which the combustion can last is larger.

However, a different tendency was observed in the case of the blends with Red-P in this study (Table III). Figure 6 clearly shows the tendency.

Two mechanisms should be taken into account. When a specimen ignites faster, the scission products spout out at lower temperature. The preliminary reactions in the polymer occur before full-scale and continuous combustion. Char formation and cross-linking reaction under the existence of red-phosphorous can be imagined.

The degradation at the initial stage seems to occur in the PS sequence and it restricts by the adjacent groups for the concentration of the dimer is lower. After the reactions occur, the chemical structure of the copolymer changes to a different structure whose heat release rate during combustion is low. So, the effect of red-phosphorous to SEBS is supposed to be the structural deformation by the preliminary reactions and the radical trap in the gaseous phase.

The similar effect was observed in the blend with BBC. As the temperature of the thermal degradation

is lower, the similar preliminary reaction occurs in this case and the lower PHRR is caused by the reactions.

Several new flame-retardants do not show attractive performance. The blend with Melamine cyanurate shows a lower rate whereas the blend burnt out in the UL test was.

The result of the UL test does not always agree with the value of the cone calorimeter. The flame-retardancy of the blend with DBDPO/Sb<sub>2</sub>O<sub>3</sub> measured by the UL test was quite different from that by the cone calorimeter test. As the mechanism of DBDPO/Sb<sub>2</sub>O<sub>3</sub> is a radical trap in the gaseous phase, the enthalpy of the oxidation reaction decreases by blending halogen compounds and it affects the flam-

TABLE V  
Scission Products of PS Blended with Three Kinds of Additives

|                                      | Amount (wt %) | Decomposition products |     |      |
|--------------------------------------|---------------|------------------------|-----|------|
|                                      |               | S1                     | S2  | S3   |
| Neat                                 | —             | 54.8                   | 0.9 | 22.6 |
| DBDPO/Sb <sub>2</sub> O <sub>3</sub> | 15            | 71.4                   | 0.9 | 8.3  |
| Red-P                                | 3             | 66.3                   | 0.4 | 10.0 |
| BBC                                  | 10            | 70.5                   | 0.2 | 15.0 |

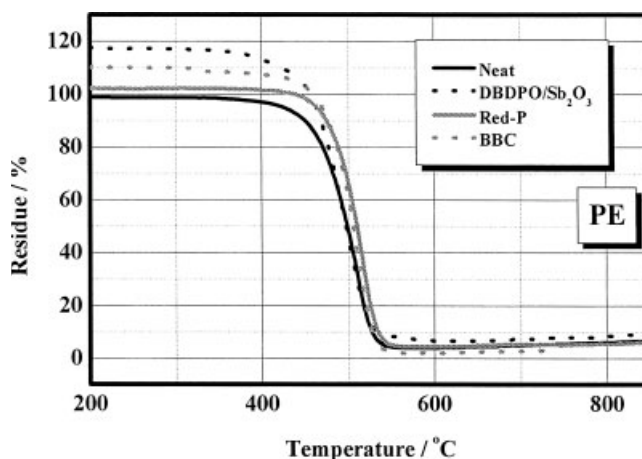


Figure 5 TGA curves of PE blended with three kinds of additives.



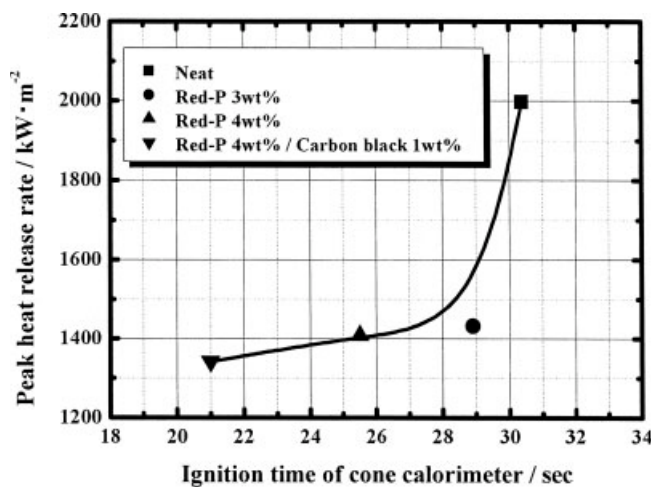


Figure 6 PHRR as a function of ignition time.

ing combustion time at the UL test because there is no external heat source.

An external heat source exists in an actual fire accident. So, the blend with DBDPO/Sb<sub>2</sub>O<sub>3</sub> is not an excellent material to protect the polymer from fires.

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